A simple cost-effective and eco-friendly wet chemical process for the fabrication of superhydrophobic cotton fabrics

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Abstract:

Superhydrophobic surfaces were created on hydrophilic cotton fabrics by a simple wet chemical process. The fabric was immersed in a colloidal suspension of zinc hydroxide followed by subsequent hydrophobization with stearic acid. The wettability of the modified cotton fabric sample was studied by water contact angle (WCA) and water shedding angle (WSA) measurements. The modified cotton fabrics exhibited superhydrophobicity with a WCA of 151° for 8 μL water droplet and a WSA of 5 to 10° for 40 μL water droplet. The superhydrophobic cotton sample was also characterized by field emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDX). The method is simple, eco-friendly and cost-effective and can be applied to large area of cotton fabric materials. It was shown that superhydrophobicity of the fabric was due to the combined effect of surface roughness imparted by zinc hydroxide and the low surface energy of stearic acid.

Keywords:

Superhydrophobic; cotton fabric; water contact angle; roughness; microstructure

1. Introduction

Superhydrophobic surfaces with water contact angles (WCA) higher than 150° are inspired by natural surfaces such as the lotus leaf, on which water drops remain almost spherical and easily roll off, removing dirt particles in their path [1,2]. Such surfaces have great potential for numerous scientific and industrial applications. Studies have shown that superhydrophobicity arises due to the combined effect of hierarchical micro- and nanostructures of the surfaces as well as from the low surface energy of the materials [3]. Therefore, SH surfaces can be prepared either by creating roughness on the surface of low surface energy materials or by lowering the surface energy of a rough material. Waterproofing of textiles may be considered as one of the potential applications for the superhydrophobic effect [4-16,18-21,24]. Superhydrophobic textiles would be useful for any kind of application where textile surfaces are exposed to the environment.

Even though there are several publications referring to possible textile applications, there are only few reports that actually pertain to superhydrophobic textiles. It has been reported that application of polysiloxanes by certain methods can provide nanostructures on fabrics with microstructures resulting in superhydrophobicity [4,5]. Zimmermann et al have prepared superhydrophobic textile fabrics by a gas phase coating procedure by which a layer of polymethylsilsesquioxane nanofilaments with special surface geometry was grown onto different types of textile fibers [5]. However, most of the other reported methods are based on using silica nanoparticles for creating roughness and low surface energy materials such as polysiloxanes [6,7], fluorochemicals [8,9], or long chain alkyl silanes [10-12] for hydrophobic modification. Water repellent property

can be obtained by using polysiloxanes for hydrophobization. However, fluorochemicals have to be incorporated for achieving fabrics with both water and oil-repellent property [7-9]. Superhydrophobic water-repellent cotton fabrics have been prepared by treating cotton with silica nanoparticles and a cost-effective commercial water-repellent agent [12]. Layers of two silica nanoparticles with different shapes and sizes were synthesized via a sol–gel process and used to create micro nano roughness required for achieving superhydrophobicity [12,13]. Superoleophobic textiles were obtained by incorporating perfluoroalkyl groups onto the surface of cotton modified with two layers of silica microparticles and nanoparticles covalently bonded to the fiber. However, fluorochemicals have certain disadvantages such as high cost, potential risk for human health as well as environmental concern. Another important requirement for fabric processing is that the technique should be simple and inexpensive and the resulting coatings should be nontoxic and have good chemical and environmental stability.

Superhydrophobic antibacterial fabrics have been fabricated by embedding silver or copper particles and modification of the particle-containing cotton textiles with alkylsilanes [14,15]. Very recently, superhydrophobic surface on cotton substrates has been prepared by dip-coating in Al sol, and modifying with sodium stearate [16]. However, zinc oxide (ZnO) is well-known for its antibacterial properties and is generally regarded as a safe material for humans; further it is easy to prepare and cost-effective compared to silver and copper nanoparticles. ZnO nanoparticles have been immobilized on fabrics via ultrasound irradiation to render them with anti-bacterial property [17]. Superhydrophobic surfaces on cotton substrate have also been created using ZnO nanorod arrays and subsequent hydrophobic modification with a long chain alkyl silane

like n-dodecyl trimethoxysilane [18,19]. Xu et al have prepared superhydrophobic cotton fabrics by fabricating rough surfaces using silica nanoparticles and ZnO nanorod arrays together with subsequent modification with long chain alkyl silane [19]. Cotton fabrics have also been functionalized with ZnO thin films by pulsed laser deposition to change their wettability [20]. Recently, superhydrophobic and ultraviolet-blocking cotton textiles have been fabricated by a tedious treatment involving various complex processes steps such as ZnO seeding, hydrothermal growth of ZnO nanorods, layer-by-layer deposition of a silica shell on the surface of ZnO nanorods, and hydrophobic modification with octadecyltrimethoxysilane [21].

In the present work, we have employed a facile wet chemical process to render the cotton fabrics superhydrophobic. The cotton fabric is immersed in a dispersion of zinc hydroxide in ethanol and hydrophobically modified by immersing in solution of stearic acid. Zinc hydroxide was synthesized by a simple precipitation method using low cost and non-toxic materials. The treated cotton samples were characterized by water shedding angle measurements, field emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDX).

2. Experimental

2.1. Materials

Zinc sulphate was purchased from SD Lab Chem Industry. Anhydrous sodium carbonate was purchased from Sarabhai M Chemicals, Baroda. Sodium hydroxide flakes and ethanol were procured from Merck. Stearic acid (n-octadecanoic acid) was purchased

from S.D.Fine-Chem Ltd. Stearic acid solution (0.05 M) was prepared by dissolving 0.70 g in 50 ml ethanol.

2.2. Preparation of treated cotton fabric samples

Zinc hydroxide was prepared by a modified precipitation method reported earlier by us and described elsewhere [22]. In brief, 50 mL of 0.10 M aqueous zinc sulphate solution was mixed with 50 mL 0.10 M sodium carbonate and 50 mL 0.10 M sodium hydroxide in a 250 mL two-necked round bottomed flask kept at 70°C in a water bath while stirring vigorously. The stirring was continued for further 30 min while maintaining the temperature constant at 70°C. The precipitated zinc hydroxide was separated by centrifugation and repeatedly washed with distilled water and ethanol. The white residue of zinc hydroxide was dried under ambient conditions for several hours till a powder of constant weight was obtained.

0.10 g of zinc hydroxide was dispersed in 10 ml ethanol and ultrasonicated for 30 min to get a colloidal suspension. Clean and dry cotton fabric samples (2" x 2") were immersed in the suspension and padded with a glass rod for 10 min on each side, the cotton fabric was then dried at 60ºC for 1 h. Hydrophobic modification of the zinc hydroxide - treated cotton fabric was carried out by immersing it in 10 mL of stearic acid solution for 30 min. The modified cotton fabric was then dried under ambient conditions for 4 h and heat treated at 100ºC for 1 h in an air oven. Fig. 1 shows the schematic of the preparation of superhydrophobic cotton fabric.

For comparison, cotton fabric sample treated only with zinc hydroxide was prepared by immersing in zinc hydroxide suspension. Another cotton fabric sample was treated with zinc stearate by immersing in zinc stearate suspension prepared by stirring 0.10 g each of zinc

hydroxide and 0.14 g stearic acid in 10 ml ethanol. A third sample was immersed in stearic acid solution. Finally, all three treated fabrics were dried at 100ºC for 1 h. Similarly, samples of zinc hydroxide, zinc stearate and stearic acid coatings on glass slides were also prepared.

2.3. Characterization

The crystalline structure of zinc hydroxide applied on the fabric before and after stearic acid treatment after heating at 100ºC was examined by X-ray diffraction (XRD) technique, model Rigaku D/max 2200 powder diffractometer, using Cu-Kα radiation. The diffraction patterns were scanned between 10-80^{o} in steps of 0.02º at 2º/ min scan speed. The surface morphology of the fabric sample was studied using field emission scanning electron microscope, FESEM model Carl Zeiss Supra 40. Energy dispersive spectrometer (EDS), from Oxford Instruments was used for the elemental analysis of the surface. Surface roughness of the fabrics was measured by using 3D profilometer, model Nano Map 500LS from AEP Technology, USA.

Water contact angles (WCA) of the fabric samples were measured using contact angle analyzer, model Phoenix 300 Plus from M/s Surface Electro Optics, South Korea. Tangent fitting mode is used in this instrument for the determination of WCA. The drop volume was 8 μL. WCA measurement was difficult for the rough textile surface because of the difficulty in the reliable determination of the substrate baseline. However, five measurements of WCA were taken and the mean value was reported. The usual practice of sliding angle measurement was not suitable for the cotton fabric with textile fibers sticking out of the fabric surface. Therefore we have adopted the new technique of measuring water

shedding angle (WSA) developed by Zimmerman et al to evaluate the water repellent properties of superhydrophobic textiles [5]. WSA was determined by releasing a drop of water onto the inclined substrate from a defined height and measuring the minimum angle of inclination at which the drop completely rolls off the surface.

3. Results and Discussion

XRD studies of the as-prepared zinc hydroxide and its modified form have been described in our previous work [22]. It was shown that the as prepared zinc hydroxide consisted mainly of ε-zinc hydroxide and small amounts of ZnO. The XRD of stearic acid modified zinc hydroxide had exhibited peaks due to zinc stearate. The XRD patterns of the untreated and the stearic acid modified coatings on the fabric are shown in Fig. 2. Most of the peaks in the diffractogram in Fig. 2 (a) were consistent with the values in the standard of JCPDS card for ZnO (JCPDS No. 5-0664) and can be indexed to the hexagonal ZnO with wurtzite structure. XRD pattern also revealed a few minor peaks of ε-zinc hydroxide (JCPDS No. 12-479) and zinc carbonate hydroxide $Zn_5(CO_3)_2(OH)$ (JCPDS No. 19-1458). This indicates that major part of the zinc hydroxide is converted to ZnO after heat treatment at 100ºC. XRD of stearic acid modified coating in Fig. 2(b) was nearly identical to the XRD patterns of untreated zinc hydroxide except for the peaks appearing between 20 to 25^o which are identified as the peaks due to zinc stearate (JCPDS No. 5-0079).

3.1. Wettability studies of the treated cotton fabrics

WCA and WSA of untreated and treated cotton fabric samples are shown in Table 1. Fig. 3 shows images of water drop on untreated cotton and cotton samples treated with zinc hydroxide and stearic acid, zinc hydroxide only, stearic acid only and zinc stearate. It can be seen that the untreated fabric was hydrophilic and water drops gradually spread on the surface so that WCA and WSA could not be measured. On the other hand, the water drops on fabrics treated with zinc hydroxide and stearic acid were spherical and WCA values were higher than 150º and water drops rolled on tilting slightly. WSA was <10º. Even on fabric treated with zinc hydroxide only, water drops were nearly spherical initially with WCA >140º and WSA of about 15º but WCA decreased steadily if the water drop was allowed to be in contact with the fabric surface for longer periods and eventually the water drops were sticking to the surface. In the case of cotton fabric treated with stearic acid only, WCA was 106º and water drops slided at WSA >45º. Even though stearic acid is a low surface energy material and cotton fabric has roughness, their combination was not sufficient to achieve superhydrophobicity probably due to the random orientation of the long chain fatty acid, one end of which has polar hydrophilic hydroxyl groups. For fabric sample treated with zinc stearate, the average WCA was 140º with WCA higher in some areas and lower in other areas on the fabric surface. Thus a single immersion step in zinc stearate suspension to create superhydrophobic fabric was not advantageous. Fig. 4 shows the photographs of cotton fabric samples with water droplet on them.

It was also found that heat treatment of the samples after stearic acid modification improved the water repellent properties. Samples dried under ambient temperature had higher WSA of 25 ± 5º. Similarly, solvent also had an effect. If zinc hydroxide dispersion was prepared with water, the treated cotton samples had lower WCA. Thus water repellent properties of the treated fabric are influenced by the process parameters such as zinc hydroxide treatment, solvent medium, stearic acid immersion, as well as drying temperature.

3.2. Surface microstructure of the treated cotton fabrics

Optical micrographs of untreated, zinc hydroxide -treated + stearic acid modified and zinc stearate treated cotton fabric samples are shown in Fig. 5. It was seen that the fibers of the woven fabric treated with zinc hydroxide and modified with stearic acid exhibited a thin uniform layer over the fibers retaining the gaps and voids between the woven structure, almost similar to that of untreated fabric whereas the zinc stearate treated fabric showed thick and non-uniform coverage of white deposit filling most of the voids in the woven fabric. The adhesion of the white deposit was not good and peeled on rubbing the fabric. Therefore, the fabric treated with zinc hydroxide and modified with stearic acid was better than zinc stearate treated fabric. The microscale surface roughness of the treated fabric was determined by using 3D profilometry. 2D profile and 3D profile of 3

mm x 3 mm area of the superhydrophobic cotton fabric obtained by treatment with zinc hydroxide and stearic acid are shown in Fig. 6. The average roughness (R_a) was 24.7 μm and rms roughness (R_q) was 30.8 μm. The maximum peak height and valley depth were about 65 μm and 70 μm respectively.

Fig. 7 shows FESEM images of zinc hydroxide coating (before and after modification with stearic acid) applied on a smooth substrate like a glass slide and dried at 100ºC for 1 h. Zinc hydroxide coating showed a porous microstructure and displayed stacks of nanosheet-like structure at higher magnification. After stearic acid modification, there was a difference in microstructure as reported earlier [22]. FESEM images of zinc hydroxide -treated + stearic acid modified cotton fabric sample are shown in Fig. 8. The deposit of particles on the fibers can be clearly seen at lower magnification. The surface exhibited a morphology which resembled stacks of flaky sheets at higher magnification. Each sheet had an average width of 250 to 500 nm and length of 1 μm to several microns. The microstructure at high magnification is similar to the sheet like structure of zinc stearate reported earlier [22,23]. The sheets and flakes created hierarchical micro nano roughness on the fabric surface. Thus modified fabric showed a microstructure with double-scale micro-nano roughness. XRD of stearic acid modified zinc hydroxide also had indicated the formation of zinc stearate.

EDX analysis of the large area on the treated fabric and the white deposit embedded on the cotton fiber was carried out to determine the zinc content of the modified fabric. The results are shown in Fig. 9 and Table 2. It was found that Zn, O and C were present at both locations indicating the presence of zinc stearate, ZnO. C and O present in cellulose of the cotton fabric may also contribute to their content. The average Zn content of the modified fabric surface was about 14 wt%. The atomic ratio of Zn:O:C was 1:10:20 for large area and 1:20:40 on the deposit. Atomic ratio of Zn:O:C in zinc stearate is 1:4:36. Therefore, the larger C content on the deposit indicates the higher zinc stearate content at that location.

In most of the reported work on superhydrophobic fabrics, fluorochemicals are employed for hydrophobic surface modification [7-9,13]. Xue et al have used a complex coating of amino- and epoxy-functionalized silica nanoparticles on epoxy-functionalized cotton textiles to generate a dual-size surface roughness, followed by hydrophobization with stearic acid and fluoroalkylsilane [8]. Fluorinated silanes are too expensive to be applied for the surface modification of cotton fabrics. Further, most fluorinated materials may cause serious risks for human health when the treated cotton fabric comes in contact with skin and also while handling during the treatment process. Therefore, it is necessary to avoid the usage of fluorochemicals. In the present study, a safe, cheap and eco-friendly fatty acid like stearic acid was used for hydrophobic surface modification.

Very recently, Lee et al have prepared SH surfaces by spin coating commercially available ZnO nanoparticles onto a surface with chemical modifications [24]. They found that surface roughness and WCA increased with number of coating cycles and therefore, 15 coating cycles were required to get sufficient surface roughness for achieving

superhydrophobicity. The spin coating method is not feasible for large area application on the fabric surface. In the present work, a single immersion in zinc hydroxide suspension followed by stearic acid modification was sufficient to impart sufficient roughness and the process has the potential to be scaled up for application on large areas.

The superhydrophobic property of the treated fabrics was stable for several months under ambient conditions. In order to check the durability of the superhydrophobic property in contact with water, the samples were immersed in water for several hours and it was found that the fabric was not wetted by water and water drops rolled on their surface.

3.3. Correlation of wettability with surface roughness of the treated cotton fabrics

A superhydrophobic surface is obtained by two criteria: a low surface energy and an appropriate surface roughness which results in water detaching from the surface at a low roll-off angle. Therefore, the fabrication process of the superhydrophobic cotton fabric can be divided into two steps: (i) the formation of rough surface on the fabric by immobilizing zinc hydroxide; and (ii) the chemical modification with low surface energy stearic acid. It was found that both steps are indispensable for achieving a good superhydrophobic surface.

Even though cotton fabric surface is rough, modification with low surface energy stearic acid resulted in an increase of WCA to 106º only compared to WCA of 75º of a stearic acid film on a smooth surface. Immersion of the fabric in zinc hydroxide served to obtain double scale micro-nano roughness as well as the formation of zinc stearate on the surface so that the long chain alkyl chains are extended outwards.

To further understand the wettability of the interface between the treated cotton surface and a water droplet, Cassie's equation [25] can be employed.

$$\text{Cos } \theta^c = f_1 \text{ Cos } \theta_e - f_2 \qquad (1)$$

where θ^c is the apparent WCA, θ_e is the equilibrium WCA, f_1 and f_2 are the fractional interfacial areas of the rough surface and of the trapped air in the voids respectively such that ($f_1 + f_2 = 1$). As lots of air gets trapped into the asperities on the rough surface, a water drop contacts the top of the asperities preventing the water droplets from penetrating into the hollows and troughs, leading to superhydrophobicity. Substituting for $f_2 = (1 - f_1)$, equation (1) becomes

$$\text{Cos } \theta^c = f_1 (\text{Cos } \theta_e + 1) - 1 \qquad (2)$$

Substituting for $\theta^c = 151^\circ$, and $\theta_e = 75^\circ$ (WCA on a smooth glass surface coated with stearic acid), f_1 was estimated to be 0.10 and hence, f_2 was 0.90. Therefore, water droplets on the surface would be in contact with 90% of air and 10% of fabric surface.

Initial WCA of zinc hydroxide –only treated fabric was 140º due to the hierarchical roughness as shown in Fig. 7(a) and (b) but the surface undergoes transition from Cassie state to Wenzel state in which water penetrates into the asperities on the surface. This might be due to the hydrophilic nature of zinc hydroxide and the active hydroxyl groups present on its surface.

The Wenzel model also explains how roughness contributes to the wetting behavior of a surface [26]. In Wenzel's approach, the contact angle at a rough surface can be described as

$$\text{Cos } \theta^{w} = r \cos \theta_e \qquad (3)$$

where θ^{w} is an apparent contact angle on a Wenzel surface, and r is the ratio of the total wet area of a rough surface to the apparent surface area in contact with the water droplet. When there is no trapped air, the surface behaves as a Wenzel rough surface, and f_1 is identical to the value of r in the Wenzel model.

4. Conclusions

The hydrophilic cotton fabric was transformed to superhydrophobic surface by a simple immersion process. The essential criteria such as an appropriate surface roughness and low surface energy required to obtain superhydrophobic surface on cotton fabric were achieved by immersion in a suspension of zinc hydroxide and stearic acid solution which resulted in WCA of 151º and WSA of <10º. The hierarchical micro-nano roughness on the treated cotton fabric was provided by zinc hydroxide and low surface energy was attained by stearic acid modification. This combined effect is responsible for the superhydrophobicity of the treated fabric. The simplicity of the process of coating onto fabrics makes it possible for potentially large scale production. The materials used are cheap and safe and the method is free of any fluorochemicals.

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Figures

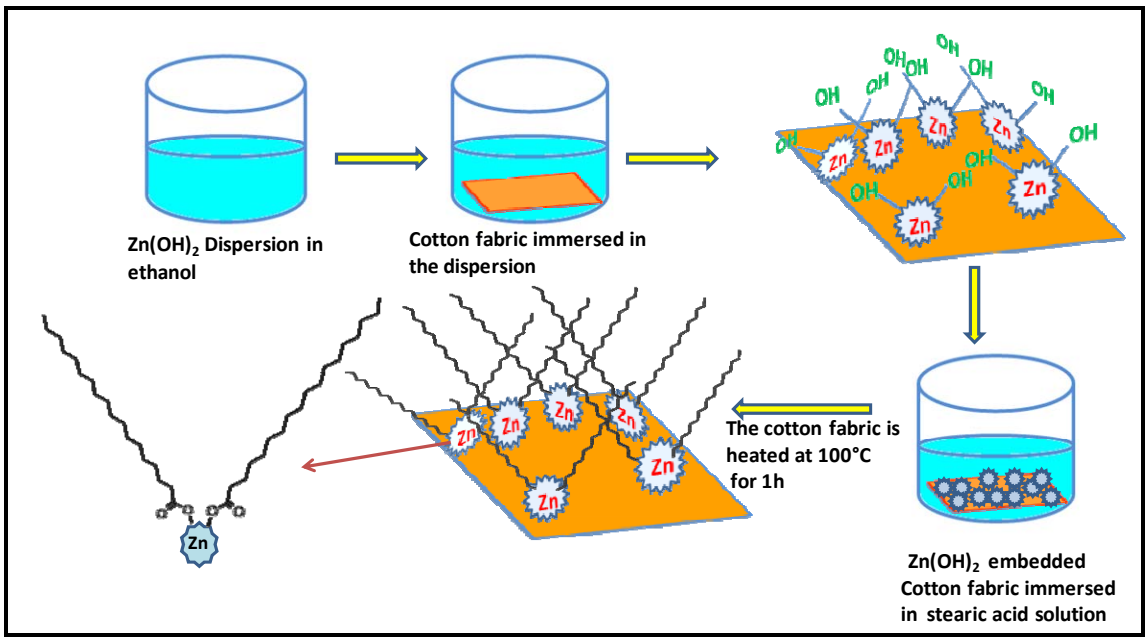
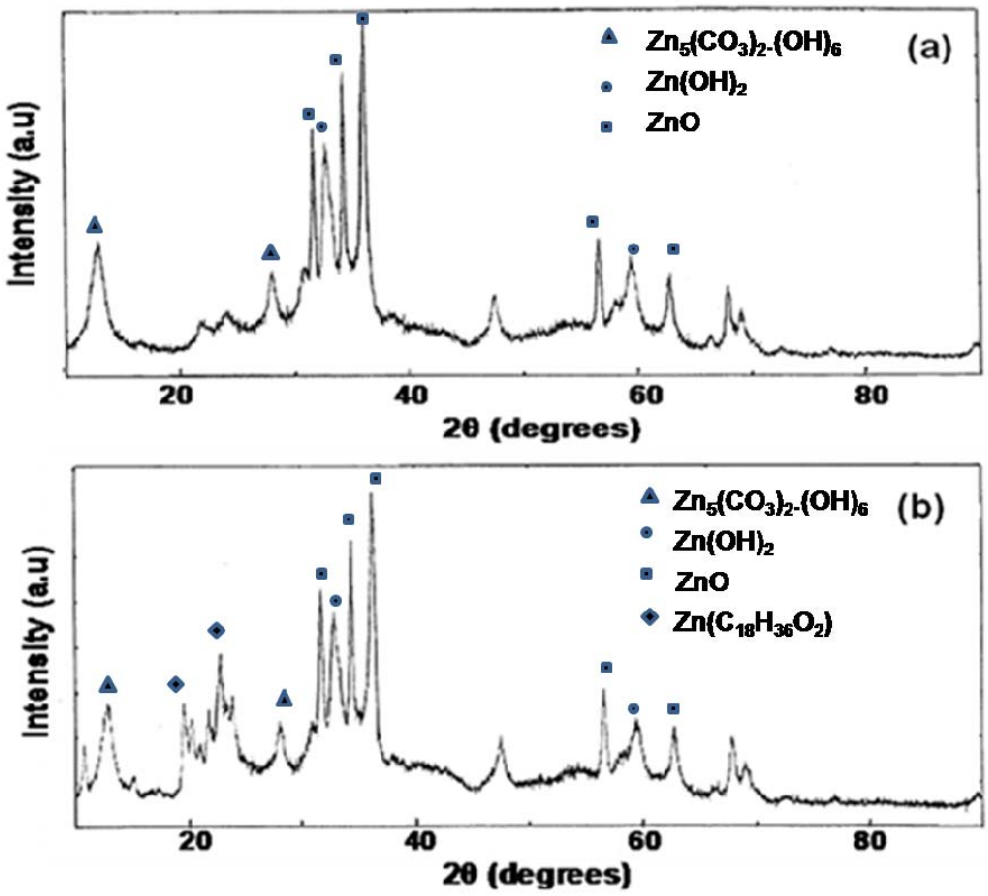


Fig. 1.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ZnO
(a)
20
40
60
80
2θ (degrees)
Intensity (a.u)
$Zn_5(CO_3)_2(OH)_6$
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ZnO
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(b)
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60
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2θ (degrees)

Fig. 2.

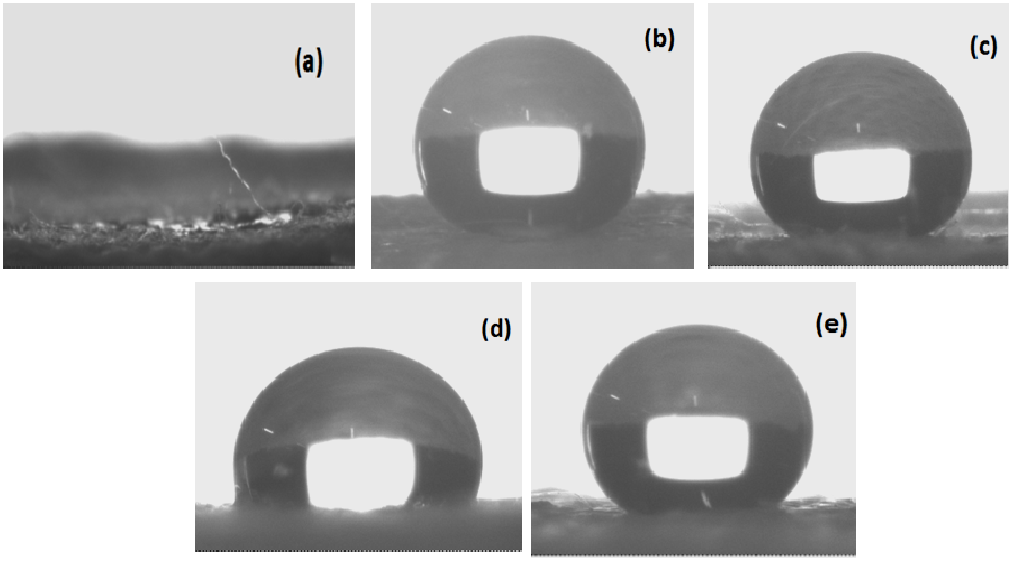

Fig. 3.

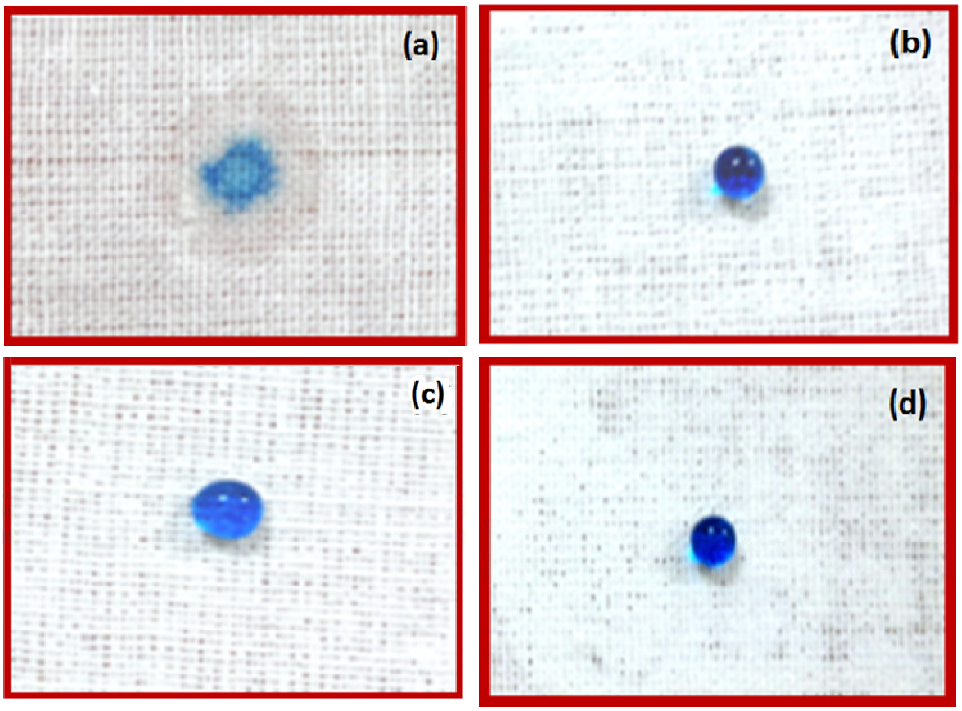

Fig. 4.

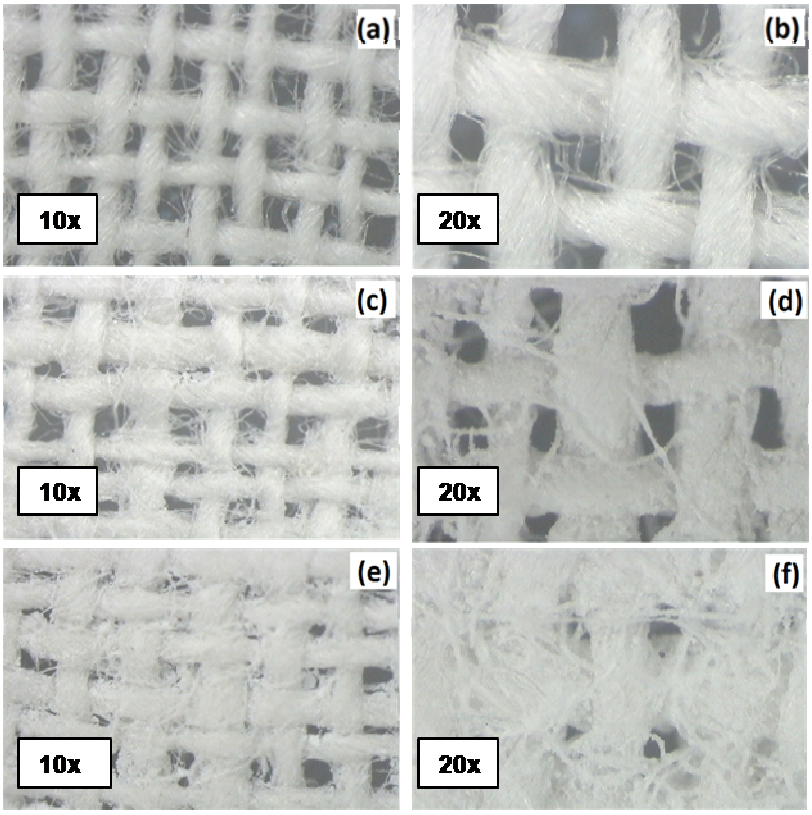
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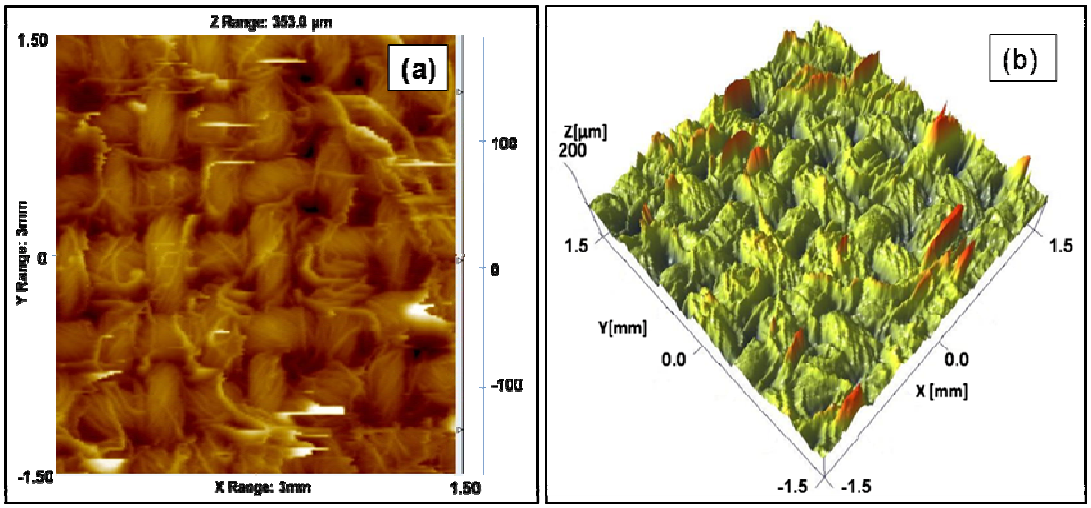
Fig.5.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-1.50
X Range: 3mm
1.50
100
0
-100
(b)
Z[µm]
200
1.5
Y[mm]
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-1.5
1.5
0.0
X [mm]
-1.5

Fig. 6.

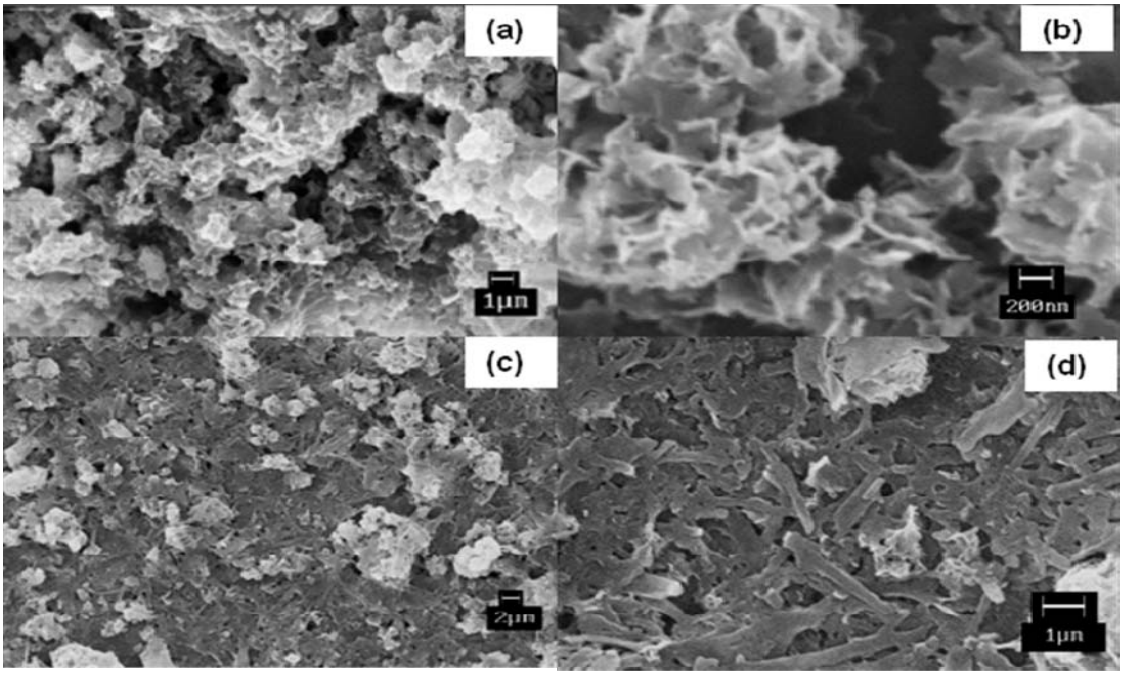

Fig. 7.

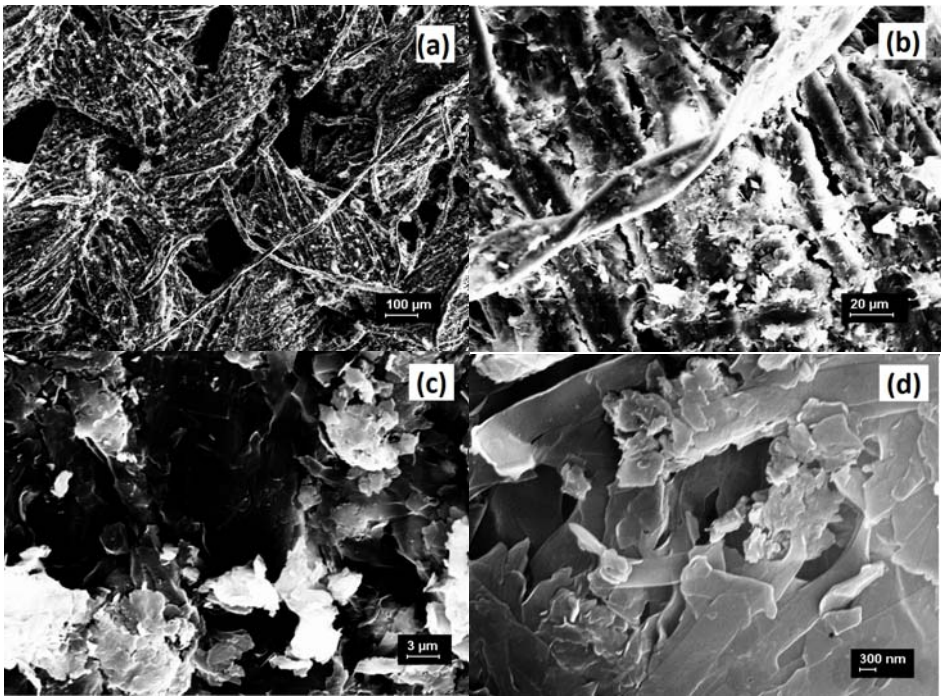

Fig. 8.

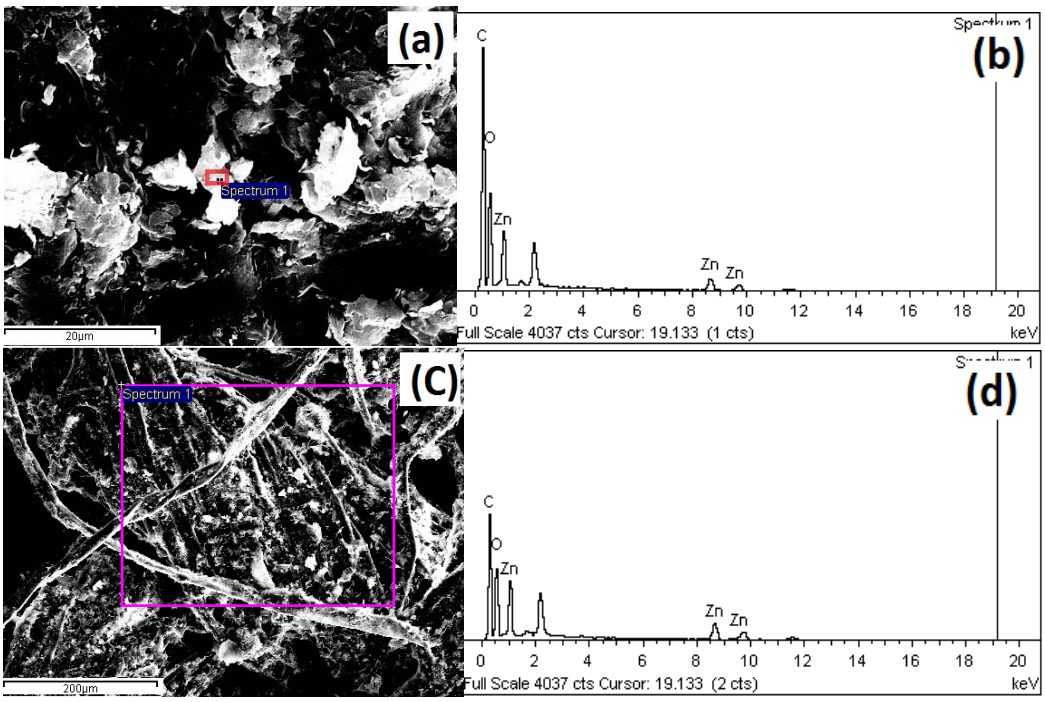

Fig. 9.

Table 1

WCA and WSA of the untreated and treated cotton fabric samples

Sample	WCA (°)	WSA (°)
Untreated	<10	-
Zinc hydroxide treated	142 ± 5	20 ± 5
Zinc hydroxide treated + stearic acid modified	151 ± 3	7 ± 2
Stearic acid treated	106 ± 5	> 45
Zinc stearate treated	140 ± 3	25 ± 5

Table 2

Chemical composition of the superhydrophobic cotton surface by EDX analysis

Location		Element		
		Zn	O	C
Large area	Wt %	13.91	35.24	50.85
	Atomic %	3.20	33.13	63.68
White deposit	Wt %	7.57	36.41	56.01
	Atomic %	1.64	32.26	66.10

Figure Captions:

Fig. 1. Schematic of the preparation of superhydrophobic cotton fabric by immersion in ethanolic $Zn(OH)_2$ followed by immersion in stearic acid solution.

Fig. 2. X-ray diffraction patterns of the films of (A) zinc hydroxide powder, and (B) stearic acid modified zinc hydroxide.

Fig. 3. Images of water drop on different cotton fabrics, (a) untreated, (b) treated with zinc hydroxide and stearic acid, (c) zinc hydroxide only, (d) stearic acid only and (e) zinc stearate.

Fig. 4. Photographs of samples of cotton fabrics with colored water drop on them; (a) untreated, (b) treated with zinc hydroxide and stearic acid, (c) zinc hydroxide only, and (d) zinc stearate.

Fig.5. Optical micrographs of samples of (a,b) untreated cotton fabric, (c,d) fabric treated with zinc hydroxide and stearic acid, (e,f) treated with zinc stearate suspension; Magnifications: (a,c,e) 10x and (b,d,f) 20x.

Fig. 6. 2D profile (a) and 3D profile (b) of superhydrophobic cotton fabric treated with zinc hydroxide and stearic acid

Fig. 7. FESEM images of (a,b) as prepared zinc hydroxide and (c,d) after modification with stearic acid; (b) and (d) are higher magnifications of (a) and (c).

Fig. 8. FESEM images of superhydrophobic cotton fabric; Magnifications (a) 150 x, (b) 1.0 Kx, (c) 5.0 Kx and (d) 25.0 Kx.

Fig. 9. EDX spectra (b,d) of superhydrophobic cotton fabric on white deposit (a) and large area (c).